

REMARKS

Cancelled Claims

Applicants have cancelled non-elected Claims 1-39.

Allowable Subject Matter

Applicants note with appreciation the allowance of Claims 40-50, and the finding of Claims 52-64 to be allowable if rewritten in independent form.

Rejection under 35 U.S.C. §102(b)

The Examiner has rejected Claims 51-65 under 35 U.S.C. 102(b) as being anticipated by Banin '453. The Examiner has not provided any further information about the basis for the rejection except to point generally to portions of Banin, *i.e.*, abstract, column 1, lines 55-67, column 2, lines 1-12, lines 40-67, column 3, lines 7-53, column 4, lines 10-25, lines 61-67, column 5, lines 1-2, lines 34-48, column 6, lines 25-43, column 8, lines 15-45, column 9, lines 15-63.

In the interest of moving prosecution along, Applicants have amended independent Claim 51 to recite a nanorod barcode, comprising a first **linear** segment of a first material and a second **linear** segment of a second material joined longitudinally to the first segment, wherein at least one of the first and second segments is capable of generating emission in response to excitation energy.

The sections of Banin as cited by the Examiner are reproduced below. The emphases have been added.

1. Abstract

"The present invention provides a new method for the production of inorganic semiconductor nanocrystals having a rod-like shape. More specifically the present invention provides a method of synthesizing rod shaped Group III-V semiconductor nanocrystals. The method comprises: reacting, in a high-boiling point organic solvent, a two-source precursor solution comprising at least one metal source and at least one nonmetal source, or a single-source precursor solution, with a metal catalyst or an agent capable of producing said metal catalyst, said high-boiling point organic solvent having a temperature above 200°C., thereby forming a reaction product comprising semiconductor nanocrystals of various shape; cooling the reaction product, and subsequently exposing said cooled reaction product to at least one centrifugal step so as to obtain semiconductor nanocrystals having substantially rod-like shape.

The rod-shaped nanocrystals obtained by the method of the invention usually have organic ligands as a coating on their outer surfaces. Such organic ligands affect the solubility of the particles and may be substituted or removed,

according to the application intended for said particles after the reaction is completed."

Banin taught a method of synthesizing rod shaped Group III-V semiconductor nanocrystals thereby forming a reaction product comprising semiconductor nanocrystals of various shape. He did not state that the method taught "a nanorod barcode, comprising a first linear segment of a first material and a second linear segment of a second material joined longitudinally to the first segment" as recited by amended independent Claim 51. Banin did teach that the method involves "a two-source precursor solution". As is known in the art, formation of nanotube structures often involves using a variety of chemical precursors to produce a nanotube structure made of only one material.

2. Column 1, lines 55-67, Column 2, lines 1-12

Miniaturization of electronic and optical devices requires semiconductors of nanometer size domain. Inorganic semiconductors, in particular Group III-V semiconductors, exhibit features that make them attractive for use in solid state electronics as well as optical devices (e.g., high thermal stability, high electron mobility, low energy band gap, and direct-band gap behavior.

Developing preparation methods of semiconductor nanocrystals has been an important branch of synthetic chemistry. For many of the semiconductors, syntheses through the reaction of simple reactants have been proved to be impossible, thus only until recent years, some of them can be prepared through the use of organometallic precursors in organic solvents. The typical examples are Group III-V semiconductor nanocrystals, which are formed by dissolving a Group IIIa precursor and a Group Va precursor in a solvent and then applying heat to the obtained mixture of solvent and precursors. More specifically, Group III-V semiconductor nanocrystals may be produced by using silyl cleavage. Specifically, Group III halides have been reacted with E(SiMe₃)₃, where E=P,As, in hydrocarbon solvents to yield nanocrystalline III-V semiconductors [1].

In this section Banin made no specific teaching about nanorods. The idea that multiple precursors (i.e., a Group IIIa precursor and a Group Va precursor) were used to make specific types of nanocrystals (i.e., Group III-V semiconductor nanocrystals) is further evidenced. A Group III-V semiconductor is a semiconductor made of one material not a first material and a second material as recited in Claim 51. The material is a compound comprising a component from Group III and a component from Group V. Such a nanocrystal is not the structure recited in amended Claim 51 - "a nanorod barcode, comprising a first linear segment of a first material and a second linear segment of a second material joined longitudinally to the first segment".

3. Column 2, lines 40-67

The diameters of the nanowires could be tuned by changing the size of the catalyst clusters [9] and for silicon nanowires, the smallest diameter reported was 6 nm. For InAs and other III-V semiconductor nanowires, the average diameters are larger than 10 nm. Such diameters are at the onset of the strong quantum confinement regime providing rather limited band gap tunability by size effects. A whole set of optoelectronic devices including transistors, detectors and a light emitting diode were demonstrated using these nanowire building blocks [10, 11]. Micron long silicon nanowires with diameters of 4-5 nm were also prepared in a pressurized solution system by using gold nanocrystals as catalyst [12].

Rod-shaped nanocrystals are interesting because the rod shape produces polarized light emission leading to polarized lasing [13, 14]. Additionally, rod-shaped particles are suitable for integration into nano-electrode structures for the production of electronic devices such as sensors, transistors, detectors, and light-emitting diodes [11, 15]. A recent example of rod-shaped nanocrystals was described in relation with CdSe nanocrystals [16, 17]. Shape control in this case was realized by kinetically controlled growth along the special c-axis of wurtzite CdSe nanocrystals through the use of a mixture of surfactants. Such a process is not applicable for the growth of cubic-structured semiconductor nanorods, e.g. nanorods of a few important III-V semiconductors. Therefore a novel and completely different rod growth mechanism is needed for these compounds.

In this section Banin taught InAs, silicon, CdSe and other semiconductor nanowires, as separate structures. There is no teaching about nanostructures "comprising a first linear segment of a first material and a second linear segment of a second material joined longitudinally to the first segment", as recited in amended Claim 51. Banin also taught the shape of CdSe nanocrystals can be controlled during growth, but he did not teach that other materials could be introduced into the shaping; he taught only CdSe.

4. Column 3, lines 7-53

There is a need in the art to facilitate preparation of nanocrystalline semiconductors, especially Group III-V semiconductors, having rod-like shape of controlled dimensions in a controllable and repeatable manner, which are not available to date. The term "III-V semiconductor" is used to describe crystalline material or solid solution formed from the reaction of at least one metal precursor from group IIIa of the Periodic Table of the Elements (B, Al, Ga, In, and Tl) and at least one element from group Va of the Periodic Table of the Elements (N, P, As, Sb, and Bi). It should be noted here that the expression "at least one" is used in recognition of the fact that, for example, a particular Group IIIa metal precursor may be reacted with more than one particular Group Va precursor, e.g., GaAsP, and vice versa, e.g. InGaAs.

The term "nanocrystal having rod-like shape" or "nanorod" is meant a nanocrystal with extended growth along the first axis of the crystal while maintaining the very small dimensions of the other two axes, resulting in the growth of a rod-like shaped semiconductor nanocrystal of very small diameter, where the dimensions along the first axis may range from about 10 nm to about 500 nm. The nanorods prepared by the method of the invention may have one end made of non semiconducting material.

Examples of Group III-V semiconductors that may be prepared by the method of the invention are InAs, GaAs, GaP, GaSb, InP, InSb, AlAs, AlP, AlSb and alloys such as InGaAs, GaAsP, InAsP. Examples of Group II-VI semiconductors that may be prepared by the method of the invention are CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe and the like. Examples of Group I-VII semiconductors are CuCl, CuBr, CuI, AgCl, AgBr, AgI and the like.

The main idea of the present invention is based on introducing nanoparticles of a metal catalyst that serve as starting nanocrystals from which nanorods of inorganic semiconductors grow. Without being bound to theory, it is proposed that the reaction precursors dissolve in the metal nanoparticles and the semiconductor nanorods grow from these particles.

The metal catalyst can be for example a noble metal, e.g. gold, a Group IIIb metal, e.g. In, Ga, Al or a transition metal, e.g. Fe, Zn, Cd, etc. The catalyst nanoparticles may either be formed in-situ in the reaction process from one of the precursor materials by using a reducing agent or be added to the reaction process.

Again, the idea that multiple precursors (*i.e.*, a Group IIIa precursor and a Group Va precursor) are used to make specific types of nanocrystals (*i.e.*, Group III-V semiconductor nanocrystals) was taught. Banin taught that such nanocrystal compounds are not limited to two components, *e.g.*, GaAs, but such compounds can also contain additional components, *e.g.*, GaAsP, InGaAs. Banin taught a long list of compounds from which nanocrystals can be made using the method of his invention. Each compound is *one material* and makes *one nanocrystal*. Banin did not teach here, or in any other section, a method or structure comprising "a first linear segment of a first material and a second linear segment of a second material joined longitudinally to the first segment" as recited in amended Claim 51. Banin taught that metal catalyst nanoparticles are used for initiating growth of inorganic semiconductors nanorods. This is a well known method for growing nanocrystals, and does not produce nanocrystals having "a first linear segment of a first material, and a second linear segment of a second material joined longitudinally to said first segment" as recited in amended Claim 51.

Figure 1 of Banin is a schematic illustration of the growth mechanism of InAs nanorods according to the invention. Figure 1 is described further in Column 6, lines 15-24:

Thus, in a specific example, InAs nanorods were synthesized via the reaction of tris(trimethylsilyl)arsenine ((TMS).sub.3 As) and InCl.sub.3 in trioctylphosphine-oxide (TOPO). FIG. 1 shows a schematic illustration of the growth mechanism of InAs nanorods. The metallic catalyst, namely indium, forms a starting nanocrystal from which the semiconductor nanorod grows, the growing direction shown in the figure signifying that the left end portion of the rod was grown first and then "moved" away from the metallic catalyst during the continuous growth of the nanorod.

The indium catalyst particle is not a linear segment, rather it is a nanoparticle or droplet, as is discussed further in item 8 below. The catalyst particle is an artifact of the growth process and may or may not be present once the semiconductor nanorod is grown. Nevertheless, Applicants have amended Claim 51 to recite "a first linear segment of a first material and a second linear segment of a second material joined longitudinally to the first segment" to emphasize further that neither linear segment of the nanorod barcode, as recited in amended Claim 51 refers to a catalyst nanoparticle or nanodroplet.

5. Column 4, lines 10-25

The reaction precursors used in the method of the invention are selected from Group Ib, IIb or IIIa metal compounds, Group VIIa, VIa or Va non-metal compounds, Group IV element compounds, compounds comprising both Group Ib and Group VIIa elements, compounds comprising both Group IIb and Group VIa elements and compounds comprising both Group IIIa and Group Va elements. Consequently, the inorganic semiconductor rods prepared by the method of the invention are selected from Group III-V, Group III-V alloys, Group II-VI, Group I-VII, and Group IV semiconductors.

Examples for single-source precursor compounds, e.g. for Group III-V semiconductors: {t-Bu.sub.2 In[.mu.-P(SiMe.sub.3).sub.2]}.sub.2, [t-Bu.sub.2 In(.mu.-PH2)].sub.3 ; for Group IV semiconductors: (C.sub.6 H.sub.5).sub.2 SiH.sub.2).

See item 2 above.

6. Column 4, lines 61-67, Column 5, lines 1-2

Semiconductor nanocrystals are of interest for use in optical displays, optical detectors, data communication systems and biological applications such as fluorescence marking of biomolecules, and as sensors. Rod/shell nanocrystals based on the nanorods prepared by the method of the invention may provide further control of the optical and electronic properties of the nanorods

specifically as a method to enhance their fluorescence efficiency that is important for various applications [19, 20].

Banin taught rod/shell nanocrystals, not “a first linear segment of a first material and a second linear segment of a second material joined longitudinally to the first segment” as recited by amended Claim 51.

7. Column 5, lines 34-48

The method of the present invention affords the formation of nanorods of inorganic semiconductors with controlled diameters and lengths. The method is exemplified hereinbelow with reference to the preparation of InAs nanocrystal rods, which belong to the important Group IIIa-Va semiconductors. While this is a preferred embodiment, the method of the invention can be used to make any of the inorganic semiconductor nanocrystals in rod shape. Examples for Group III-V semiconductors are GaAs, GaP, GaSb, InP, InSb, AlAs, AlP, AlSb and alloys such as InGaAs, GaAsP, InAsP, etc.; examples for Group II-VI semiconductors are CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, etc.; examples for Group I-VII semiconductors are CuCl, CuBr, CuI, AgCl, AgBr, AgI, etc.; and examples for Group IV semiconductors are Si and Ge.

See item 4 above.

8. Column 6, lines 25-43

A reducing agent, for example NaBH₄, is added to in-situ create metallic indium nanodroplets that direct the one-dimensional rod growth via a solution-liquid-solid mechanism (hereinafter “SLS mechanism”). The SLS mechanism was first used in the growth of polycrystalline whiskers of III-V semiconductors reported by Buhro and coworkers [21]. The so-grown whiskers had diameters in the range of 10-150 nm and lengths of a few micrometers. In our example, the in-situ formed indium nanodroplets are much smaller than the indium droplets used in Buhro's method. These nanodroplets are mostly consumed during the nanorod growth, thus the length of the as-prepared nanorods is confined. In addition, we can control the growth effectively by controlling the reaction time. Additionally, several separation stages were introduced to obtain rods of desired length. The reactions are carried out in coordinating solvents leading to soluble rods and the reaction temperature is relatively high resulting in crystalline rods.

Banin taught that nanodroplets used as catalysts are mostly consumed during nanorod growth. These catalyst particles are not either of “a first linear segment of a first material” or “a second linear segment of a second material joined longitudinally to the first segment” as recited in amended Claim 51.

9. Column 8, lines 15-45

*In order to optimize the synthesis conditions, the effect of the ratio between the precursors and the reducing agent was studied. This ratio, marked as P, was calculated as the molar ratio between arsenic and the upper limit of metallic indium calculated from the amount of reduction agent. The inventors studied syntheses with P ranging from 1 to 9. In TOP, since the reaction temperature is lower, annealing was needed for rod growth. In this condition, nanorods were obtained when P was as high as 9 although a large fraction of the rods were kinked and their yield was low. TOPO provided higher temperatures, under which rods formed immediately upon injection of precursors. **The short reaction time means that growth of large indium nanodroplets can be mostly avoided, enabling the use of a lower ratio that results in a higher yield of rods. It was found that a ratio P of 4.5 is optimal in a typical synthesis conditions.***

Concerning the optical properties of the rods, the absorption spectrum exhibits a tail extending above 1 micron. FIG. 5 illustrates the photoluminescence spectrum of the InAs nanorods shown in FIG. 2B. Rods-toluene solution was measured using a He-Ne laser for excitation (632 .mu.m). The emission was collected as a right angle configuration, dispersed by a monochromator and detected by a InGaAs PIN photodetector with lock-in amplification. As can be seen in FIG. 5, the fluorescence maximum occurs at about 1080 nm, and this corresponds well to the known position of the band gap for InAs nanodots with a diameter of about 3.5 nm, similar to the diameter of the rod. It is known that the band gap of rods is determined mostly by the diameter and hardly depends on length as has been studied for CdSe nanorods [13].

Banin taught against retaining large indium catalyst nanodroplets and preferred to be rid of them. Thus the indium catalyst nanodroplets cannot be either of "a first linear segment of a first material" or "a second linear segment of a second material joined longitudinally to the first segment", as recited in amended Claim 51. Banin did teach photoluminescence InAs nanorods, but he did not teach "a first linear segment of a first material and a second linear segment of a second material joined longitudinally to the first segment, wherein at least one of the first and second segments is configured to generate emission in response to excitation energy." as recited by amended Claim 51.

10. Column 9, lines 15-63

The method of the present invention may be easily extended to the preparation of nanorods of other inorganic semiconductors. Other Group IIIa-Va semiconductors, e.g. InP or GaAs, can be prepared using tris(trimethylsilyl)arsine/phosphine and InCl_{sub.3} or GaCl_{sub.3} as precursors. Alloy rods can also be made in a similar fashion by proper mixing of the InCl_{sub.3} and GaCl_{sub.3} precursors (or (TMS)_{sub.3} As/P) although the alloy

composition will then also be determined by the different solubility of the different precursors in the catalytic metal particle.

*Use of other catalytic metal nanodroplets having higher melting point may also provide controllable nanorod growth. As an example, the preparation of CdSe nanorods is described. Gold nanoparticles were used to catalyze and direct the growth of CdSe quantum rods. Thiol stabilized spherical gold nanocrystals have the advantage of size tunability from as small as 1 nm to tens of nanometers, narrow size distribution, and solubility in multiple solvents. Considering that the melting point of nanoparticles is reduced significantly with decreased sizes, the melting point of gold nanoparticles of appropriate sizes fall into the working temperatures of the method of the present invention, thus enabling the formation of high quality quantum rods with tunable diameters and lengths. Thus, gold nanoparticles with a diameter range of 1 to 10 nm were prepared separately [22]. These nanoparticles were made soluble in nonpolar solvents such as toluene. In the synthesis, gold nanocrystals were added either in the stock solution containing the precursors, or in the growth solution, which is TOP or TOPO or their mixtures. The reactants, dimethyl cadmium (CdMe.sub.2, with a concentration range of 0.05-0.5 M) and selenium, are dissolved in TOP or tributylphosphine (TBP), with a CdMe.sub.2 to Se ratio in the range of 0.8:1 to 1.4:1. The ratio between CdMe.sub.2 and gold, which is critical in determining the rod length, was in a range between 5:1 and 9.5:1. The reaction was conducted by injecting the stock solution into the growth solution at an elevated temperature of about 280.degree. C., followed by annealing at a temperature of about 260.degree. C. for a period from a few minutes to a few hours. **There were obtained CdSe quantum rods.** Centrifugation steps may be used to improve the length distribution. The rods have a gold nanoparticle at one end and the rod diameters can be tuned from about 1 to about 10 nm, and lengths from 10 to 500 nm.*

Rod/shell nanocrystals based on InAs nanorods, e.g. InAs/ZnSe or InAs/CdSe, may be prepared to improve the photoluminescence quantum yield and to provide further control of the optical and electronic properties of the nanorods [19, 20].

See items 4 and 6 above.

Applicants respectfully traverse the rejections and submit that Banin failed to teach each and every feature of amended independent Claim 51.

Dependent Claims 52-64 each depend from independent Claim 51 and therefore include all the features and limitations thereof. Furthermore, the dependent claims add further distinguishing features of particular utility. Accordingly, Applicants submit that the dependent claims are not anticipated over Banin.

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CONCLUSIONS

In view of the foregoing remarks, Applicants submit that the application is in condition for allowance. If, however, some issue remains which the Examiner feels may be addressed by Examiner's amendment, the Examiner is cordially invited to call the undersigned for authorization.

Please charge any additional fees, including fees for additional extensions of time, or credit overpayment to Deposit Account No. 120690.

Respectfully submitted,
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